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<p>(21) International Application Number: PCT/EP93/01530</p> <p>(22) International Filing Date: 14 June 1993 (14.06.93)</p> <p>(30) Priority data: TO92A000672 3 August 1992 (03.08.92) IT</p> <p>(71) Applicant (for all designated States except US): NOVA-MONT S.p.A. [IT/IT]; Foro Buonaparte, 31, I-20121 Milano (IT).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : BASTIOLI, Catia [IT/IT]; Via della Noce, 63, I-28100 Novara (IT). BELLOTI, Vittorio [IT/IT]; Via Mora e Gibin, 9, I-28010 Fontaneto d'Agogna (IT). LOMBI, Roberto [IT/IT]; Via Fara, 51, I-28100 Novara (IT). NICOLINI, Matteo [IT/IT]; Via Borgomanero, 82, I-28012 Cressa (IT).</p>		<p>(74) Agent: ZANOLI, Enrico; Spherilene S.r.l., Via Principi Eugenio, 1/5, I-20155 Milano (IT).</p> <p>(81) Designated States: AU, CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LI, MC, NL, PT, SE).</p> <p>Published With international search report.</p>
<p>(54) Title: BIODEGRADABLE POLYMERIC COMPOSITION</p> <p>(57) Abstract</p> <p>A polymeric composition comprises a matrix including a starch component and at least one synthetic thermoplastics polymeric component in which a filler is dispersed, characterised in that the matrix includes a fluidising agent selected from the group consisting of C₁₂-C₂₂ fatty acids, C₁₂-C₂₂ fatty alcohols, esters and amides of the said fatty acids, polyolefin waxes and polyglycol ethers of alditols or polyglycerols esterified with the said fatty acids and their mixtures and the said filler comprises natural fillers of an organic nature dispersed in the matrix in quantities of from 5 % to 70 % by weight with reference to the total weight of the composition.</p>		

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BIODEGRADABLE POLYMERIC COMPOSITION

The present invention relates to a biodegradable polymeric composition of the type including starch and synthetic thermoplastics polymers, suitable for the production of biodegradable articles having satisfactory physical and mechanical properties, by means of conventional techniques applied to thermoplastics materials of synthetic origin.

Thermoplastics compositions of the type specified above are known and available commercially and are described, for example, in patent applications EP-A-0 032 802, EP-A-0 327 505, WO 90/10671, EP-A-0 400 532, EP-A-0 404 723, EP-A-0 404 727, EP-A-0 404 728, WO 91/02024, WO 91/02025 and US 5,095,054.

Typically these compositions can be obtained by the mixing of a starch component with a synthetic thermoplastics polymeric component in conditions typical of the "extrusion-cooking" process, that is in the presence of a limited quantity of water (typically 5-40% by weight with reference to the starch-water system) or of a plastisizer at a high enough temperature and pressure to destroy the crystalline structure of the starch and to obtain a molten thermoplastics mass.

The object of the present invention is to provide

compositions of the type specified above which have improved mechanical properties, particularly a higher rigidity, even in the presence of high humidity, and properties of processability comparable with those of conventional plastics, while retaining or surpassing the rate of biodegradability of the known compositions.

This object is achieved by virtue of a polymeric composition comprising a matrix including a starch component and at least one synthetic thermoplastics polymeric component in which a filler is dispersed, characterised in that the matrix includes a fluidising agent selected from the group consisting of:

C_{12} - C_{22} fatty acids, C_{12} - C_{22} fatty alcohols, esters and amides of the said fatty acids, polyolefin waxes and polyglycol ethers of alditols or polyglycerols esterified with the said fatty acids and their mixtures and the said filler comprises natural fillers of an organic nature dispersed in the matrix in quantities of from 5% to 70% by weight with reference to the total weight of the composition.

The materials constituting the fillers are preferably selected from wood flour, walnut shells, cellulose, cotton, jute, raffia, rice chaff, animal bristles, chitin and granular starch and their mixtures; of these the preferred are the fibrous materials. The dimensions of the fillers may vary within wide limits according to the

mechanical properties which it is intended to bestow. Typically the average dimensions are between 0.5 and 500 microns, preferably between 1.5 and 300 microns; the shape ratio L/D is generally between 1 and 100 and preferably between 2 and 50.

The preferred filler concentrations are in the range 20%-50% by weight with reference to the weight of the composition. In combination with the natural organic fillers listed above, the compositions may include inorganic fillers such as talc, mica, titanium dioxide, aluminium oxide in concentrations preferably no higher than 5% by weight. The fillers may be surface treated to improve their affinity with the matrix material, for example, by means of linking agents such as titanates or zirconates or by silanisation.

The preferred matrix materials include the starch component and the synthetic thermoplastics component typically in a ratio of from 1:9 to 9.8:0.2, preferably from 1:4 to 4:1 and more preferably from 1.5:1 to 1:1.5.

The starch used is generally a natural starch extracted from various plants such as maize, potato, tapioca and cereals; it is intended that the term starch should be understood to include starches with a high amylopectin content (waxy starches) and chemically and physically modified starches, such as for example starches whose

acid values have been reduced to between 3 and 6, starches in which the type and concentration of cations associated with the phosphate groups have been modified, ethoxylated starches, starch acetates, cationic starches, oxidated starches and cross-linked starches.

As the polymeric component, the polymers described in the patent literature mentioned in the introduction to the present specification may be used.

The synthetic polymeric component is preferably selected from the following polymers and copolymers and their mixtures:

- (A) Polyvinyl alcohol, polyvinyl acetate and copolymers of an olefin selected from ethylene, propylene, isobutene and styrene with one or more monomers selected from acrylic acid, methacrylic acid, C_1 - C_4 alchylacrylate, C_1 - C_4 alchylmethacrylate, vinyl alcohol, vinyl acetate and maleic acid, such as ethylene-acrylic acid, ethylene-vinyl alcohol, ethylene-vinyl acetate, ethylene-maleic anhydride copolymers and their mixtures; the particularly preferred compounds are ethylene-vinyl alcohol copolymers with an ethylene content of from 10-44% by weight produced by the hydrolysis of the corresponding poly-ethylene-vinyl acetate with a degree of hydrolysis of between 50 and 100;
- (B) Thermoplastics polyesters such as, in particular,

homopolymers and copolymers of hydroxyaliphatic acids having from 2 to 24 carbon atoms, preferably 2⁵ to 8 carbon atoms, the corresponding lactones or lactides and polyesters derived from bifunctional carboxylic acids with aliphatic diols.

- (C) Graft copolymers of polysaccharides and their derivatives, such as starches, cellulose, modified cellulose, rubbers, alginates, pectins, dextrans and pullulans with monomers such as styrene, methylmethacrylate, methylacrylate, butylacrylate, butadiene, isoprene, acrylonitrile; graft copolymers of polysaccharides are described in the Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, Volume 3, 1986. In particular, in group B the preferred polymers and mixtures of polymers selected are:

B1) poly-epsilon-caprolactone, copolymers of epsilon-caprolactone with isocyanates such as, in particular, 4,4'-diphenylmethane diisocyanate, toluylene diisocyanate, isophorone diisocyanate or hexamethylene diisocyanate;

B2) polymers of lactic acid or polylactides, of glycolic acid or polyglycolides, copolymers of lactic acid and glycolic acid;

B3) polyhydroxybutyrate, polyhydroxybutyrate/valerate;

B4) polymers derived from dicarboxylic acids with aliphatic diols such as, in particular, polyethylene and polybutylene adipate or sebacate;

B5) block or graft copolymers formed between homopolymers and copolymers of hydroxyacids, in particular poly-epsilon-caprolactone, and one or more of the following components:

- i) cellulose or modified cellulose, for example, carboxymethylcellulose and cellulose acetate;
- ii) amylose, amylopectin, natural or modified starches;
- iii) polymers resulting from the reaction of a compound selected from aliphatic diols (such as ethylene glycol, propylene glycol, butylene glycol, polyoxyethylene glycol, polyoxypropylene glycol, neopentyl glycol, 1,4-butanediol, cyclohexanediol), prepolymers or polymers of polyesters having terminal diol groups with monomers selected from:

- bifunctional aromatic or aliphatic isocyanates,
- bifunctional aromatic or aliphatic epoxides,
- dicarboxylic aliphatic acids (such as malonic, succinic, maleic, fumaric, itaconic, glutaric, adipic, pimelic, suberic, azeleic and sebacic acids),
- dicarboxylic cycloaliphatic acids (such as cyclohexanedicarboxylic acid, 2,2,2-dicyclooctanedicarboxylic acid) or
- aromatic acids or anhydrides (such as phthalic acid),

- iv) polyurethanes, polyamides-urethanes from diisocyanates and aminoalcohols, polyamides, polyesters-amides from dicarboxylic acids and aminoalcohols, polyester-urea from aminoacids and diesters of glycols,

v) polyhydroxy polymers (such as polyvinyl alcohol, ethylene-vinyl alcohol copolymers, totally or partially hydrolysed),

vi) polyvinyl pyrrolidone, polyvinyl pyrrolidone-vinyl-acetate copolymers and polyethyloxazoline,

B6) polyesters obtained from monomers of hydroxyacids upgraded with chain lengtheners such as isocyanates, epoxides, phenylesters and aliphatic carbonates;

B7) polyesters obtained from monomers of hydroxyacids partly cross-linked with polyfunctional acids such as trimellitic acid, pyromellitic acid, polyisocyanates and polyepoxides.

More particularly, the polymers B5-B7 are useful to provide compatibility in combination with the polymers B1-B4, optionally in combination with polymers of the group A.

The matrix materials used within the scope of the invention preferably have a melt flow rate greater than 2g/10 minutes, more preferably greater than 5g/10 minutes and still more preferably, greater than 10 g/10 minutes (determined in a capillary tube having a diameter of 2.1mm and a length of 8mm at 170°C with a load of 5 kg) and preferably have a water content of from 2-10% by weight (as extruded and without conditioning).

Preferably the synthetic component of the matrix material

includes a mixture of one or more polymers from the group A) with one or more polymers from the groups B) and/or C) listed above in a weight ratio to each other preferably of from 1:6 to 6:1 and more preferably from 1:4 to 4:1.

A further component preferably used in the matrix material of the invention is a plasticizer in a total quantity of between 1 and 50% with reference to the sum of the starch component and the synthetic polymer component and preferably between 5 and 25% by weight. In the term plasticizer it is intended to include aliphatic polyols and their acetate, ethoxylate and propoxylate derivatives, in particular, glycerine, ethylene or propylene glycol, ethylene or propylene diglycol, ethylene or propylene triglycol, polyethylene glycol, polypropylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-, 1,3-, 1,4-butanediol, 1,5-pentanediol, 1,6-, 1,5-hexanediol, 1,2,6-, 1,3,5-hexanetriol, neopentyl glycol, trimethylol propane, pentaerithritol, sorbitol and their acetate, ethoxylate and propoxylate derivatives, in particular sorbitol ethoxylate, glycerol ethoxylate, pentaerithritol ethoxylate, sorbitol acetate, pentaerithritol acetate and polyvinyl alcohol; a mixture of different plasticizers may be used.

Plasticizers suitable for use are described in International patent application PCT/EP92/00320 which is incorporated in the present specification by means of its

citation.

The fluidising agents previously mentioned are particularly useful for the production of compositions with a high filler content.

These agents include fatty acids such as oleic, palmitic, stearic, linoleic, linolenic, ricinoleic, erucic acids, the corresponding fatty alcohols or esters or amides of the fatty acids listed above, in particular, mono-, di-, or tri-glycerides of the said fatty acids.

Particularly advantageous as fluidisers for the matrix material are polyglycol ethers of alditols or polyglycerols esterified with fatty acids, where the polyglycol is preferably ethylene glycol or propylene glycol, the alditol is preferably selected from sorbitol, xylitol, mannitol, the polyglycerol preferably has from 3 to 10 repeat units and the fatty acid is preferably a C_{12} - C_{22} acid, preferably saturated; preferred compounds include in particular:

- sorbitol ethoxylate mono- di- or tri-octadecanoate (CAS n. 68025-57-0) in particular poly(oxy-1,2-ethanediol), alpha-hydro-omega-hydroxy-ether with D-glucitol (3:1), tris-(Z)-octadecanoate; and
- sorbitol propoxylate mono- di- or tri-octadecanoate where the ethoxylation or propoxylation of the free hydroxyl groups may be complete or partial.

The fluidiser is typically used in concentrations of from 0.1 to 10% by weight with reference to the weight of the matrix component.

The compositions according to the invention are preferably prepared by means of the prior preparation of the matrix material including the fluidising agent or mixture of fluidising agents listed above. The preparation of the matrix material is effected by conventional processes described in the patent literature mentioned in the introduction to the present specification, that is in conditions typical of the "extrusion-cooking" process. This process comprises the mixing of the components, preferably in a heated extruder or in any device which ensures a temperature and shearing stress sufficient to render the starch material and the polymeric component compatible from a rheological point of view; in the presence of water (up to 40% with reference to the starch/water system) and/or a plastisizer at a temperature of from 80 to 210°C. The preferred method for the preparation of the matrix material comprises:

- a first stage in which the components are conveyed and/or mixed in an extruder for periods of time of the order of 2 to 50 seconds in which the starch component and the synthetic polymeric component are swelled by means of the plastisizer available and/or any water present at a temperature of between 80 and 180°C;

- a mixing stage in which the mixture is subjected to shearing stresses which correspond to similar values of viscosity of the polymeric and starch components,
- optionally, a degassing phase in which the mixture is degassed under free conditions or under controlled conditions of pressure or under vacuum to obtain a melt preferably at a temperature of from 130 to 180°C with a water content preferably less than 6% such as not to create bubbles at atmospheric pressure, for example, at the outlet from the extruder, whenever it is not wished to produce expanded products.

The melt may then be extruded directly in stranded, spaghetti-like form and in a subsequent stage the strands are mixed with the desired filler content, possibly with the addition of further fluidisers and/or plasticizers in a heated extruder to obtain an extrusion in the form of pellets suitable for conversion by conventional working processes for plastics materials.

Alternatively, the components of the matrix material and the fillers may be mixed directly in a single stage. The matrix material may also include small quantities of hydrophobic polymers in its formulation, such as polyethylene, polypropylene, polystyrene, even though, in order to maintain good characteristics of biodegradability, these polymers are preferably used in quantities no greater than 5% by weight of the total

weight of the composition.

The matrix material may further include additives such as cross-linking agents such as aldehydes, ketones, and glyoxals, process adjuvants, antioxidants, release agents, opacifiers or stabilisers.

Example 1

A two-screw/single-screw APV/V30 extruder was supplied with the following composition expressed in parts by weight:

Globe Cerestar (Registered Trade Mark) starch with an intrinsic water content of 12% by weight	40.5
EVOH (*)	30.4
EAA (**)	4.3
Erucamide	0.25
Plasticizer (***)	21.5
Fluidizer (****)	3.1
(*) poly-ethylene-vinyl alcohol, 44% molar ethylene content hydrolysis degree: 99.5 of the acetate groups	
(**) poly-ethylene-acrylic acid, 20% by weight ethylene	
(***) mixture of plasticizers: sorbitol acetate 65.5%, water 14%, glycerine 20.5% by weight, containing 0.5% of free acetic acid	
(****) sorbitol ethoxylate trioctadecanoate.	

The two-screw section of the extruder was operated with a heat profile of between 60 and 170°C.

Screw rotation: 250 rpm; screw diameter 30mm; L/D = 10.

The two-screw section was provided with an intermediate portion with a pressure of 0.9 bar.

The single-screw section was operated with a heat profile of between 150 and 140°C; screw rotation 80 rpm; screw diameter 38 mm, L/D = 16.

The extruded strands with a water content of about 5.2% by weight, were granulated and then fed to a Sandretto injection moulding press from which dumb-bell shaped test pieces (ASTM 638) were obtained which were subjected to tests to determine their mechanical properties:

- Modulus of elasticity 197 MPa
- Breaking load: 14.4 MPa
- Elongation : 656%
- MFR: 15 g/10 minutes

Example 2

The matrix material of Example 1 was used for the production of compositions including fillers according to the invention with the following formulation, expressed in parts by weight:

Matrix material: Example 1	53
Filler: wood flour (*)	40
Polyethylene wax	7

(*) maximum particle size: 200 microns

The composition listed above was supplied to a two-screw/single-screw MPC/V30 extruder operated with the following conditions:

Two-screw extruder: $L/D = 10$; $D = 10\text{mm}$; screw rotation; 250 rpm, with a heat profile between 160 and 170°C.

Single screw: $D = 38\text{mm}$; $L/D = 16$; screw rotation 50 rpm with a heat profile between 170 and 160°C.

The extruded strands were supplied to an injection press provided with a mould for forming dumb-bell shaped test pieces (ASTM 638) and the test pieces were obtained under the following conditions:

Heat profile: 155/160/165/165°C

Mould temperature: 18°C

Injection pressure: 1600 bar

Injection speed: 114cm³/s

The mechanical properties of the test pieces obtained are given in Table 1.

Example 3

The procedure of Example 1 was repeated with the use of a filler constituted by wood fibres with a maximum fibre length of about 3.5mm.

The results of mechanical tests are given in Table 1.

Example 4

The procedure of Example 2 was repeated with the

variation that a profiled section in the form of a platelet having a thickness of 5.7 mm was extruded directly from the two-screw/single-screw extruder and subjected to the determination of its mechanical properties according to ASTM 638.

The values of the mechanical properties are given in Table 1.

TABLE 1

Example	2	3	4
Breaking Load (MPa)	31.6	32.6	15
Elongation (%)	1.4	1	1
Modulus of Elasticity (MPa)	4797	5455	2846
Breaking Energy (kJ/m ²)	13.43	9.5	3

Examples 5-6

The procedure of Example 2 was repeated with the use of the following formulations expressed in parts by weight:

	EX. 6	EX. 7
Matrix material: Ex. 1	70	60
Filler: Wood Flour (*)	25	40
Polyethylene wax	5	--

The test pieces obtained from the injection moulding process were subjected to determinations of their extensibility and in all cases the results were less than 50%.

Examples 7-11

The matrix material of Example 1 was used for the preparation of formulations further including a polymer of poly-epsilon-caprolactone, in the formulations given in the table below and under the conditions described in Example 2.

Example	7	8	9	10	11
Matrix: Ex. 1	70	70	70	65	55
Wood Flour	20	--	--	25	25
Cellulose(\$)	--	20	--	--	--
Raffia (*)	--	--	20	--	--
P 300	10	--	--	--	--
P 767	--	10	--	--	10
P 787	--	--	10	--	--
glycerine	--	--	--	10	10

P 300, P 767, P 787: poly-epsilon-caprolactone

Union Carbide

(\$): Cellulose Solka Floc BW300 FCC

(*): Raffia Satralit FNT / 134-4SG

In all cases, the dumb-bell shaped test pieces obtained in accordance with Example 2 were seen to have a modulus of elasticity greater than 1000 MPa with a water content in the samples of between 4 and 5%.

The compositions according to the invention could be worked by conventional working processes for plastics

materials in particular by extrusion and injection moulding to produce shaped articles such as profiled sections and containers and expanded articles. These articles fall within the scope of the invention.

CLAIMS

1. A polymeric composition comprising a matrix including a starch component and at least one synthetic thermoplastics polymeric component in which a filler is dispersed, characterised in that the matrix includes a fluidising agent selected from the group consisting of: C_{12} - C_{22} fatty acids, C_{12} - C_{22} fatty alcohols, esters and amides of the said fatty acids, polyolefin waxes and polyglycol ethers of alditols or polyglycerols esterified with the said fatty acids and their mixtures and the said filler including natural fillers of an organic nature dispersed in the matrix in quantities of from 5% to 70% by weight with reference to the total weight of the composition.
2. A polymeric composition according to Claim 1, characterised in that the fillers are selected from the group consisting of wood flour, walnut shell flour, cellulose, cotton, jute, raffia, rice chaff, animal bristles, chitin and granular starch and their mixtures.
3. A polymeric composition according to Claim 2, characterised in that the fillers have an average size of between 0.5 and 500 microns, preferably between 1.5 and 300 microns.
4. A polymeric composition in which the fillers are

surface treated with linking agents selected from silane, titanates, and zirconates.

5. A polymeric composition according to any one of claims 1 to 4 in which the matrix material is obtained by extrusion-cooking of the starch component together with the synthetic thermoplastics polymeric component in the presence of a plastisizer and/or water.

6. A polymeric composition according to any one of claims 1 to 5, in which the synthetic component comprises:

a polymer selected from the group consisting of polyvinyl alcohol; polyvinyl acetate; copolymers of an olefin selected from ethylene, propylene, isobutene and styrene with one or more monomers selected from the group consisting of acrylic acid, methacrylic acid, alkylacrylate, alkylmethacrylate, maleic acid, vinyl alcohol and vinyl acetate; homopolymers and copolymers of hydroxyaliphatic acids having from 2 to 24 carbon atoms, the corresponding lactones or lactides; polyester polymers of bifunctional carboxylic acids with aliphatic diols; graft copolymers of polysaccharides and their mixtures.

7. A polymeric composition according to claim 6, in which the synthetic polymeric component of the matrix material includes a polymer selected from the group

consisting of polyvinyl alcohol, poly-ethylene-acrylic acid, poly-ethylene-vinyl-alcohol, polyvinyl acetate, poly-ethylene-vinyl acetate, poly-ethylene-maleic anhydride and mixtures thereof.

8. A polymeric composition according to any one of claims 1 to 6, in which the polymeric component includes one or more polymers selected from:

B1) poly-epsilon-caprolactone, copolymers of epsilon-caprolactone with isocyanates such as, in particular 4,4'-diphenylmethane diisocyanate, toluylene diisocyanate, isophorone diisocyanate or hexamethylene diisocyanate;

B2) polymers of lactic acid or polylactides, of glycolic acid or polyglycolides, copolymers of lactic acid and glycolic acid;

B3) polyhydroxybutyrate, polyhydroxybutyrate/valerate;

B4) polymers derived from dicarboxylic acids with aliphatic diols such as, in particular, polyethylene and polybutylene adipate or sebacate;

B5) block or graft copolymers formed between homopolymers and copolymers of hydroxyacids, in particular poly-epsilon-caprolactone, and one or more of the following components:

- i) cellulose or modified cellulose, for example, carboxymethylcellulose and cellulose acetate;
- ii) amylose, amylopectin, natural or modified starches;
- iii) polymers resulting from the reaction of a compound

selected from diols (such as ethylene glycol, propylene glycol, butylene glycol, polyoxyethylene glycol, polyxypropylene glycol, neopentyl glycol, 1,4-butanediol, cyclohexanediol), prepolymers or polymers of polyesters having terminal diol groups with monomers selected from:

- bifunctional aromatic or aliphatic isocyanates,
- bifunctional aromatic or aliphatic epoxides,
- dicarboxylic aliphatic acids (such as malonic, succinic, maleic, fumaric, itaconic, glutaric, adipic, pimelic, suberic, azeleic and sebacic acids),
- dicarboxylic cycloaliphatic acids (such as cyclohexanedicarboxylic acid, 2,2,2-dicycloctanedicarboxylic acid) or
- aromatic acids or anhydrides (such as phthalic acid),

iv) polyurethanes, polyamides-urethanes from diisocyanates and aminoalcohols, polyamides, polyesters-amides from dicarboxylic acids and aminoalcohols, polyester-urea from aminoacids and diesters of glycols,

v) polyhydroxylate polymers (such as polyvinyl alcohol, ethylene-vinyl alcohol copolymers, totally or partially hydrolysed),

vi) polyvinyl pyrrolidone, polyvinyl pyrrolidone-vinyl-acetate copolymers and polyethyloxazoline,

B6) polyesters obtained from monomers of hydroxyacids with chain lengtheners such as isocyanates, epoxides, phenylesters and aliphatic carbonates;

B7) polyesters obtained from monomers of hydroxyacids

partly cross-linked with polyfunctional acids such as trimellitic acid, pyromellitic acid, polyisocyanates and polyepoxides.

9. A polymeric composition according to claim 6, in which the synthetic polymeric component of the matrix material includes at least one polymer selected from the group consisting of:

A) polyvinyl alcohol, poly-ethylene-vinyl alcohol, poly-ethylene-acrylic acid, poly-ethylene-vinyl acetate, polyvinyl acetate and

at least one polymer selected from the group consisting of:

B) poly-epsilon-caprolactone, copolymers of epsilon-caprolactone, polylactic acid, polyglycolic acid, copolymers of epsilon-caprolactone with isocyanates, polyhydroxybutyrate, polyhydroxybutyrate/valerate, the ratio by weight between the polymer of group (A) and the polymer (B) being between 1:4 and 4:1.

10. A polymeric composition according to any one of claims 1 to 6, including a plastisizer selected from the group consisting of:

glycerine, ethylene glycol, propylene glycol, ethylene diglycol, propylene diglycol, ethylene triglycol, propylene triglycol, polyethylene glycol, polypropylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-, 1,3-, 1,4-butanediol, 1,5-pentanediol, 1,6-, 1,5-hexanediol,

from the group consisting of sorbitol, xylitol and mannitol.

16. A polymeric composition according to claim 14, in which the polyglycol of the fluidising agent is selected from the group consisting of polyethylene glycol and polypropylene glycol.

17. A polymeric composition according to any one of the preceding claims, in which the fluidising agent is present in quantities of from 0.1 to 10% by weight with reference to the weight of the matrix material.

18. Shaped articles made from a composition according to any one of claims 1 to 17.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/01530

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08L101/00; C08L3/00; C08L97/02; C08K5/04 //(C08L101/00,3:00)(C08L3/00,101:00)(C08L97/02,101:00)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08L ; C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,A	EP,A,0 522 358 (EMS-INVENTA AG) 13 January 1993 see page 4, line 28 - line 31 see page 4, line 50 - line 58 see page 5, line 13 - line 24 see page 5, line 37 - line 39	1,2,5,6, 10,12,18
Y	PATENT ABSTRACTS OF JAPAN vol. 16, no. 406 (C-978)(5449) 27 August 1992 & JP,A,41 36 047 (KURARAY CO LTD) 11 May 1992 see abstract	1,2,5-7, 10-14, 17,18
Y	WO,A,9 204 408 (WARNER-LAMBERT COMPANY) 19 March 1992 see page 12, line 29 - page 13, line 2 see page 13, line 24 - page 14, line 11	1,2,5-7, 10-14, 17,18
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<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
10 SEPTEMBER 1993		17. 09. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		MAZET Jean-François

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claims No.
Y	EP,A,0 327 505 (WARNER-LAMBERT COMPANY) 9 August 1989 cited in the application	1,2,5,7, 10-14, 17,18
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

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